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The Specific Refractive Index Increments for POSS Polymers in Solution.

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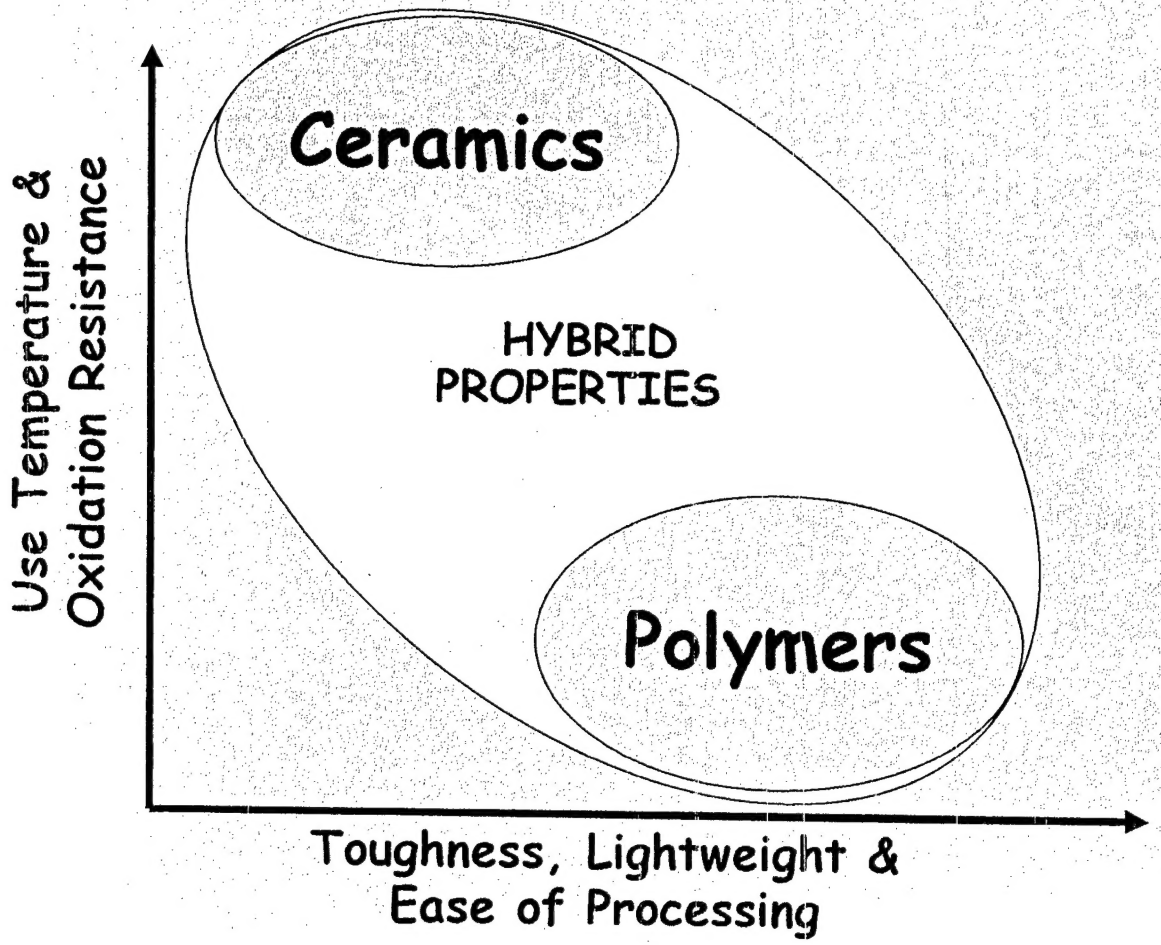
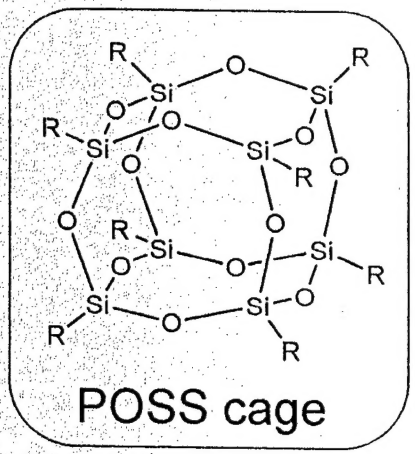
[T]ERC, Inc. – [¥]Air Force Research Laboratory

Hybrid Inorganic/Organic Polymers

Goal: Develop High Performance Polymers that REDEFINE material properties

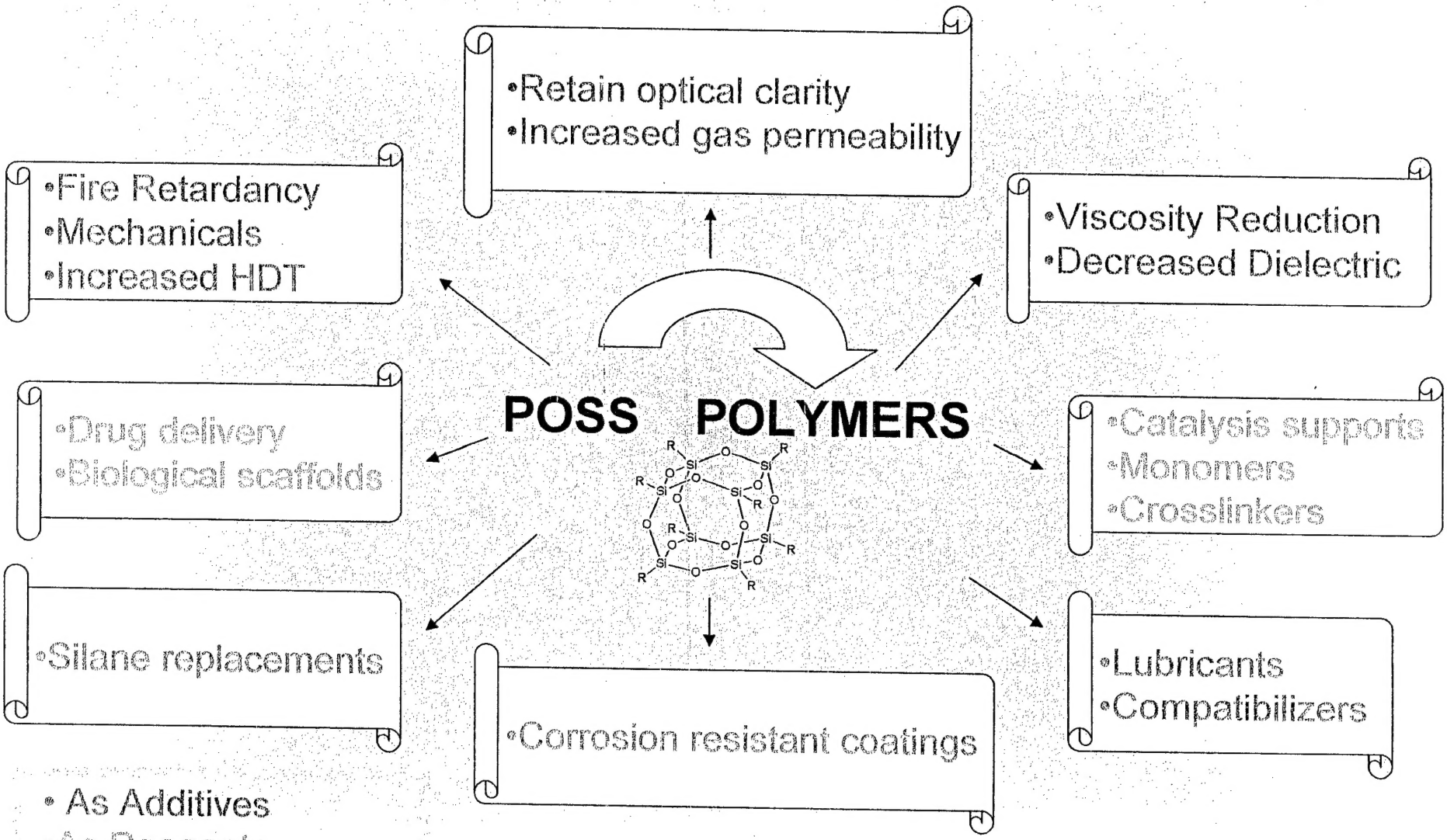
POSS – Polyhedral Oligomeric SilSesquioxanes



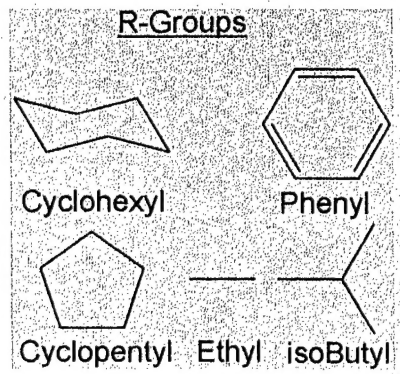


•Hybrid Plastics bridge the differences between ceramics and polymers

Introduction to POSS

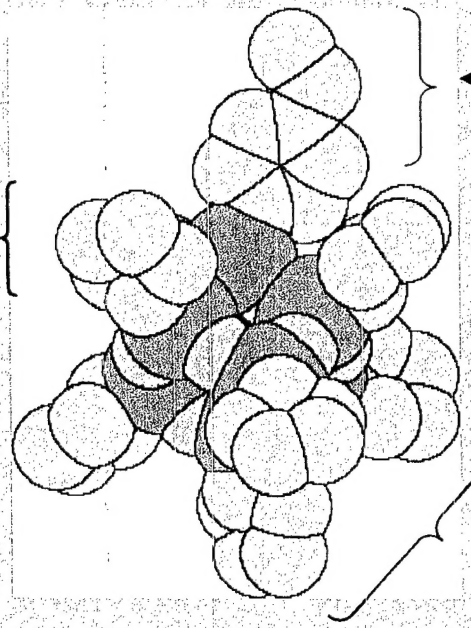


Anatomy of a POSS Nanostructure



Nonreactive organic (R) groups for solubilization and compatibilization.

Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.

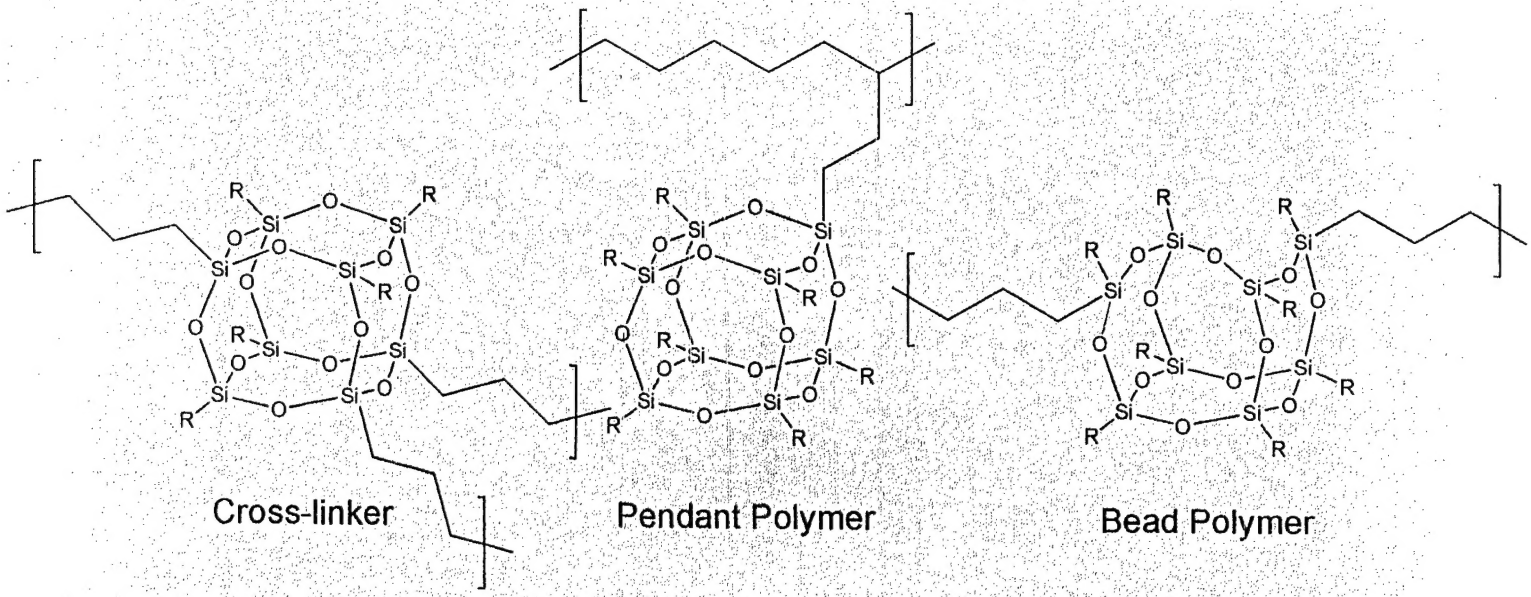


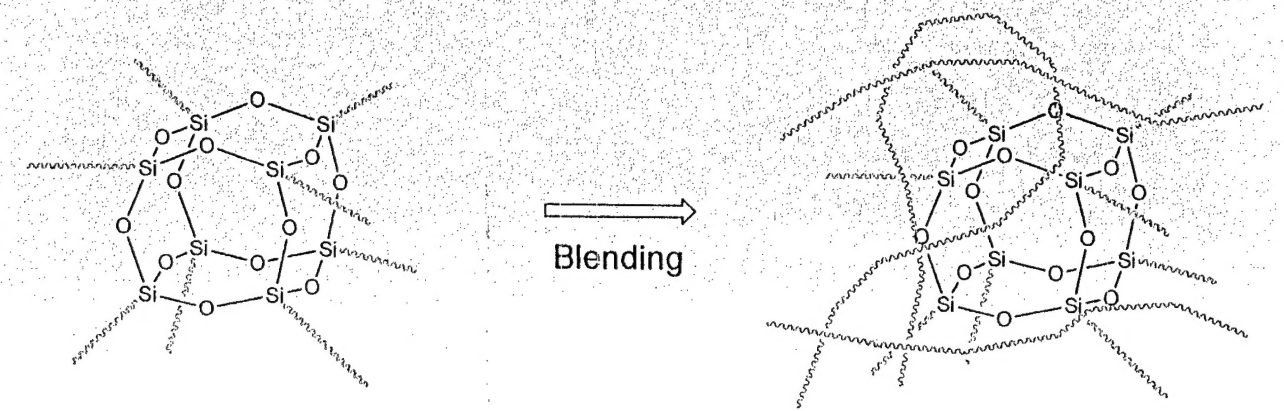
May possess one or more Functional groups suitable for Polymerization or grafting.

Thermally and chemically robust hybrid (organic-inorganic) framework.

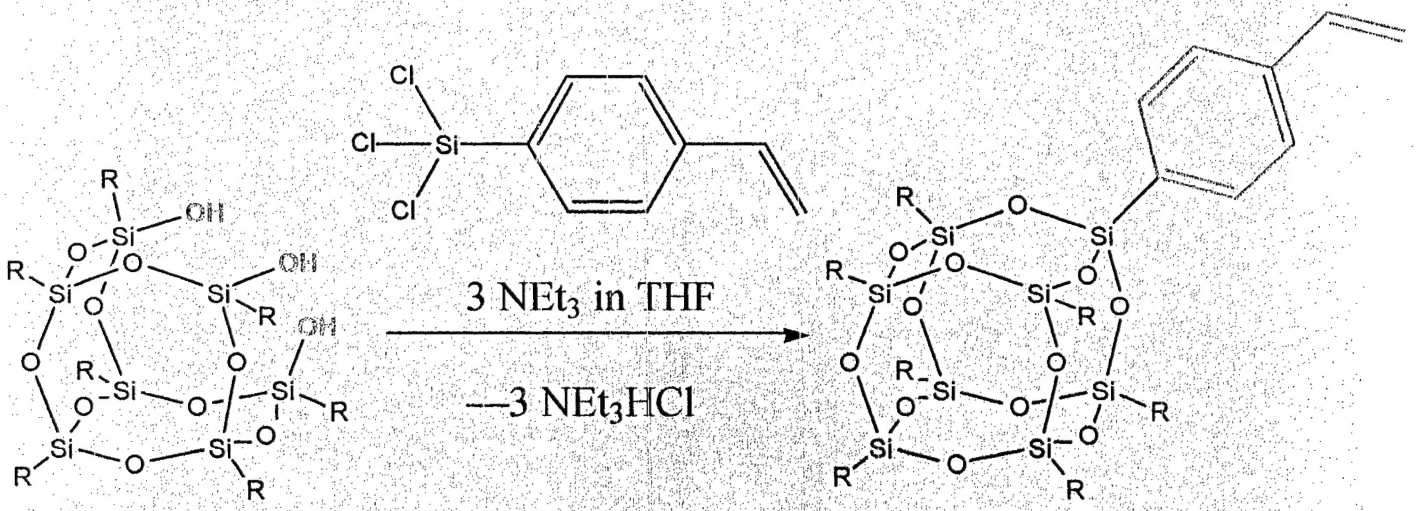
Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

POSS Polymer Incorporation



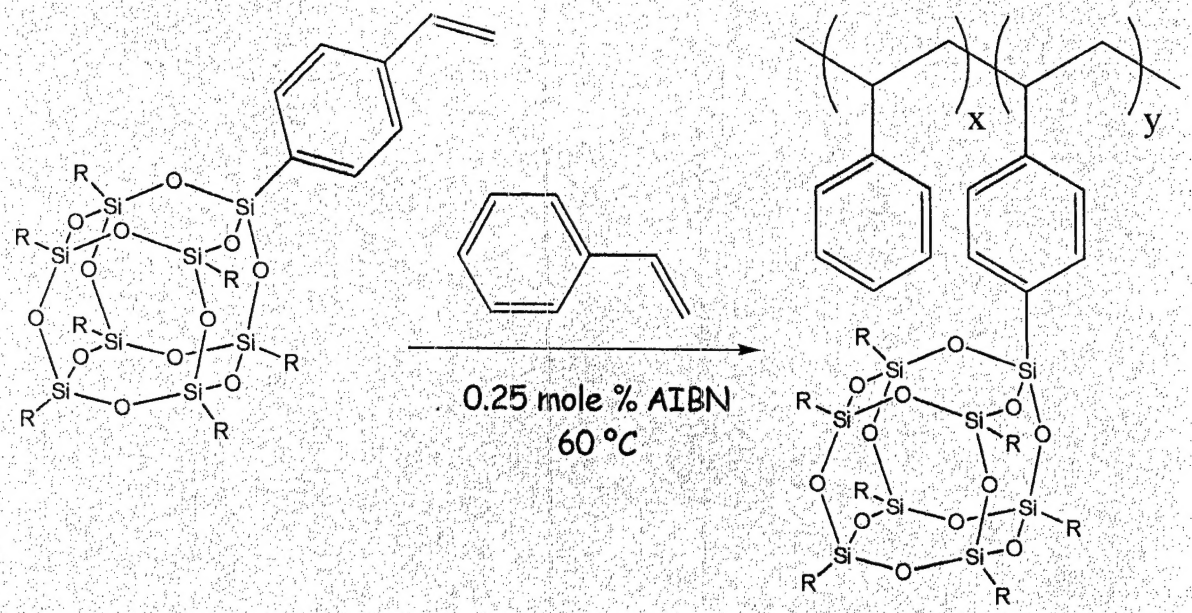


POSS Styrene Monomer Synthesis



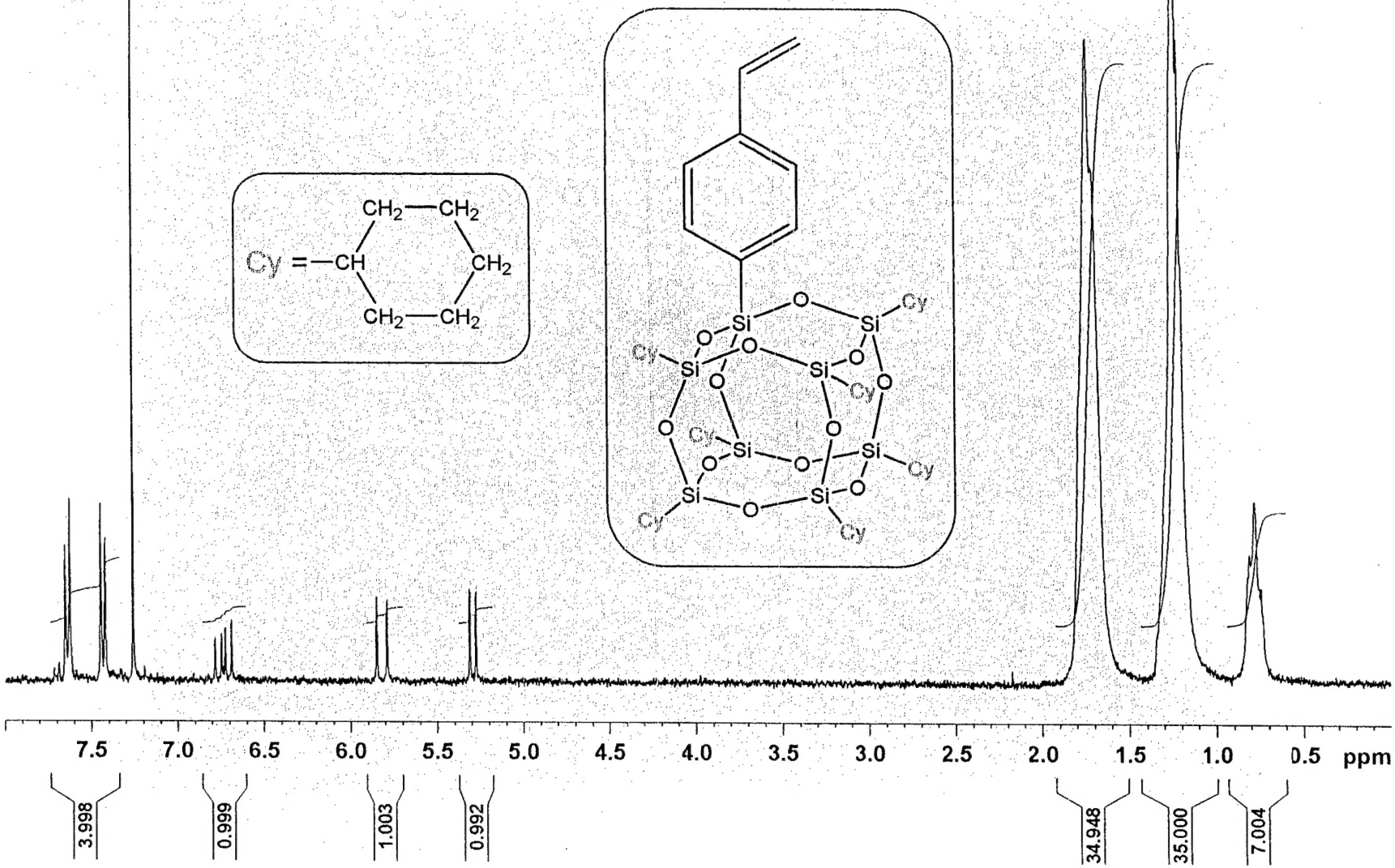
- High-yield syntheses
- Phenyl derivative requires inverse addition
- J. Inorg. Organomet. Polym., Vol 11, 2002, p. 155

POSS Styrene Copolymer Synthesis



- Solution polymerization in toluene or bulk polymerization possible
- Polymerization is limited by solubility of the POSS-macromer
- Isobutyl-POSS is the most soluble, Phenyl-POSS the least soluble
- Macromolecules Vol. 29, 1996 p. 7302

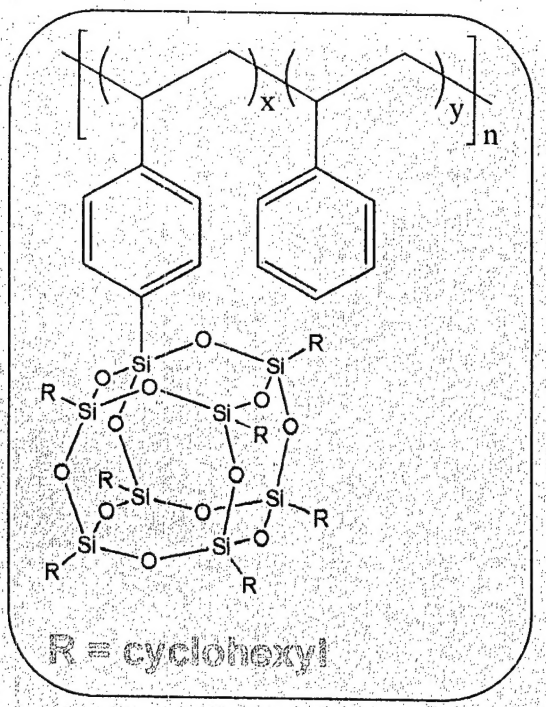
1HNMR Cyclohexyl POSS monomer



1HNMR 50wt%CyPOSS-PS copolymer

$$IR = \frac{\text{Aromatic Integral}}{\text{Aliphatic Integral}}$$

$$\text{Mole fraction POSS-styrene} = \frac{(5-3*IR)}{(63*IR+1)}$$



No monomer present.

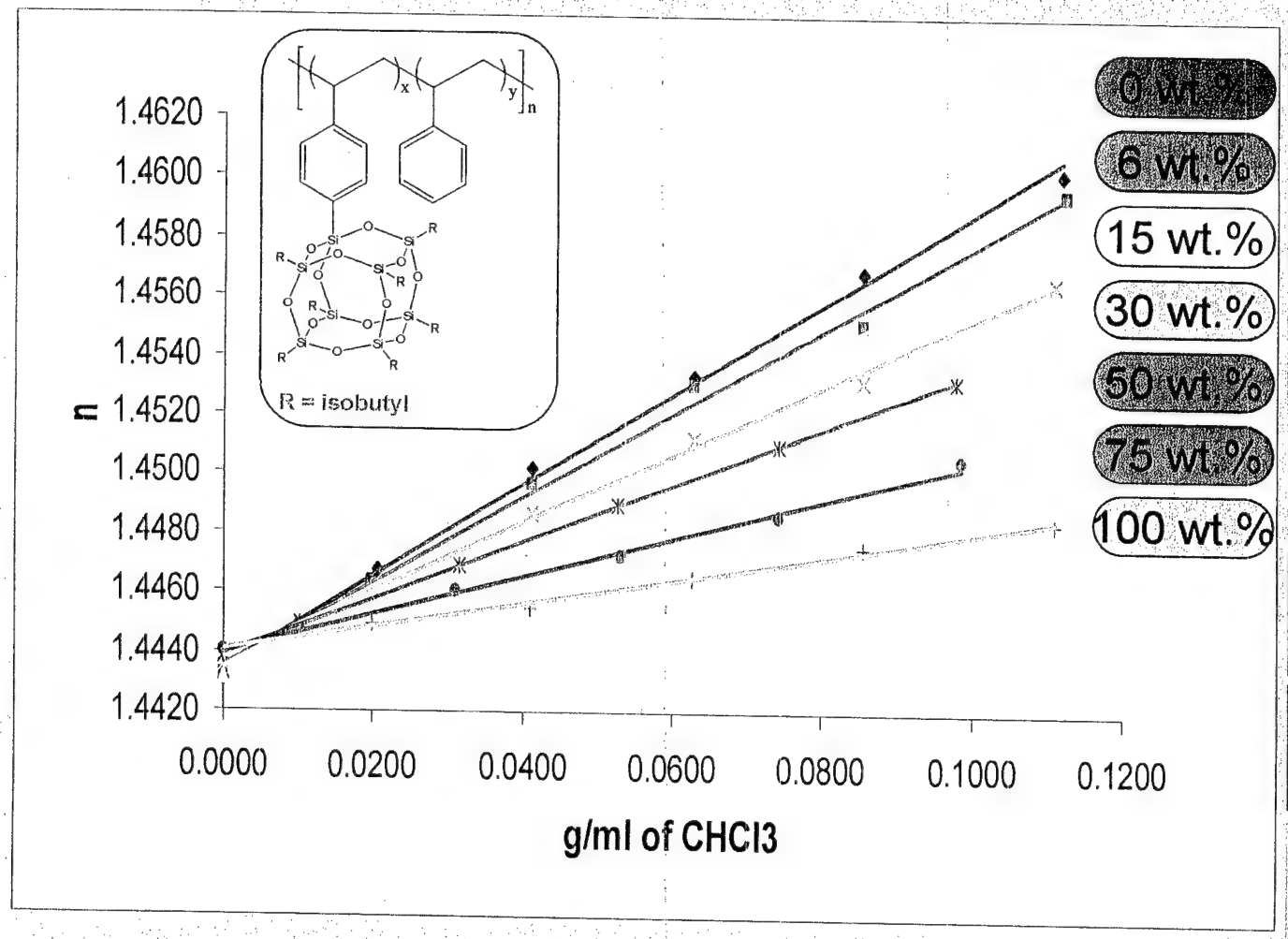
The Specific Refractive Index Increment and POSS Polymer

- The Specific Refractive Index Increment, $dn/dc = (n-n_o)/c$, is the change in RI with change in concentration.
- It is a constant value for a dilute polymer in solution at constant temperature, pressure and wavelength.
- It is useful for determining the Mw of a polymer by light scattering (GPC).
- For copolymers composed of two monomers, the dn/dc is an additive function of the individual weight fractions.

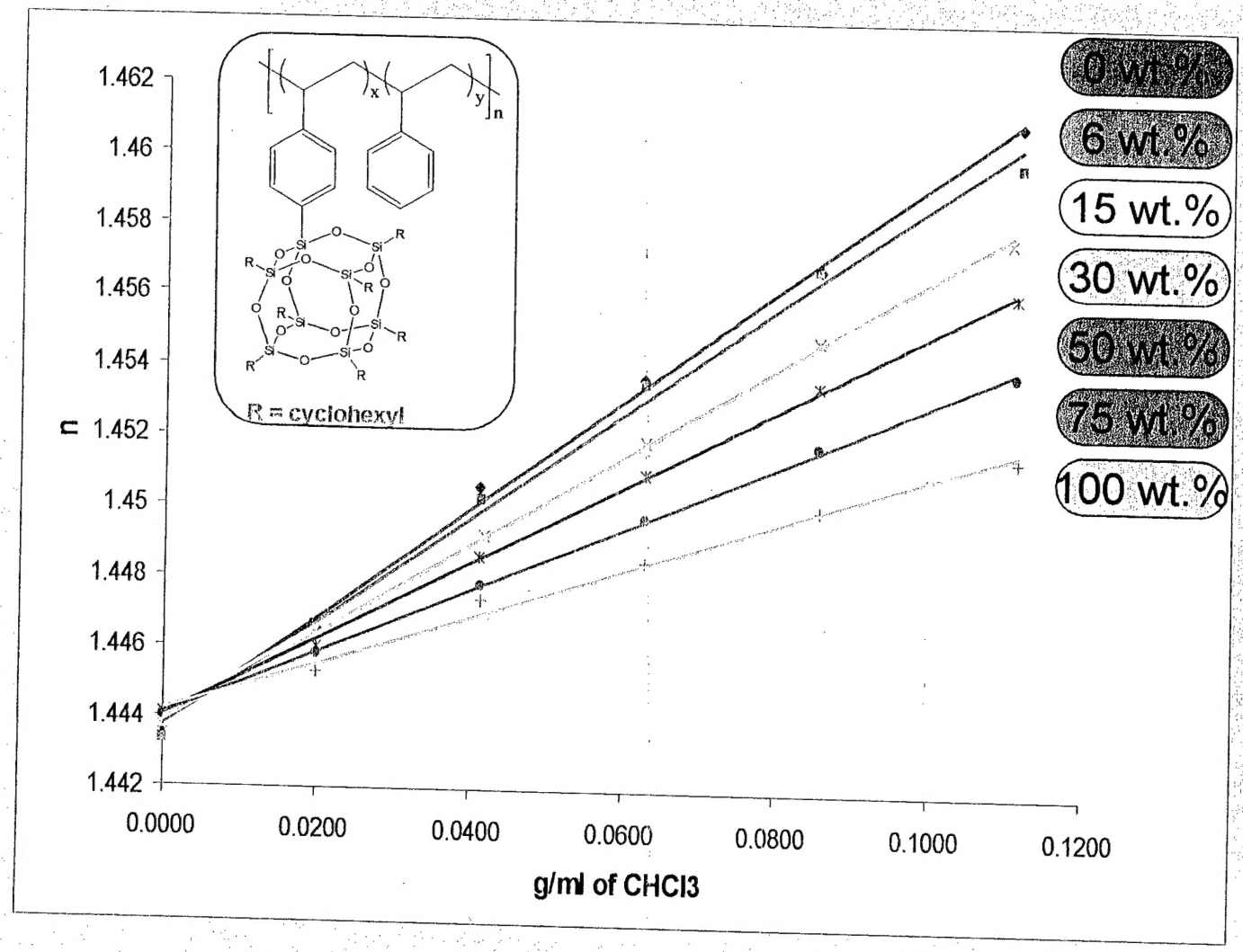
WHY FIND THE dn/dc VALUE?

- To accurately determine the weight average molecular weights of various POSS-polymers.
- To generically parameterize each POSS type (R = cyclohexyl, isobutyl, phenyl etc.) in order to predict POSS-polymer dn/dc values.
- To provide a quick and accurate method to determine POSS % incorporation in any polymer system.

RI vs. Concentration of iBuPOSS-PS copolymer



RI vs. Concentration of CyPOSS-PS copolymer



Slope = dn/dc

Y=0.1453x+1.4437
R^2 = 0.9975

Y= 0.1488x+1.4437
R^2 = 0.9949

Y=0.1352x+1.4439
R^2 = 0.9985

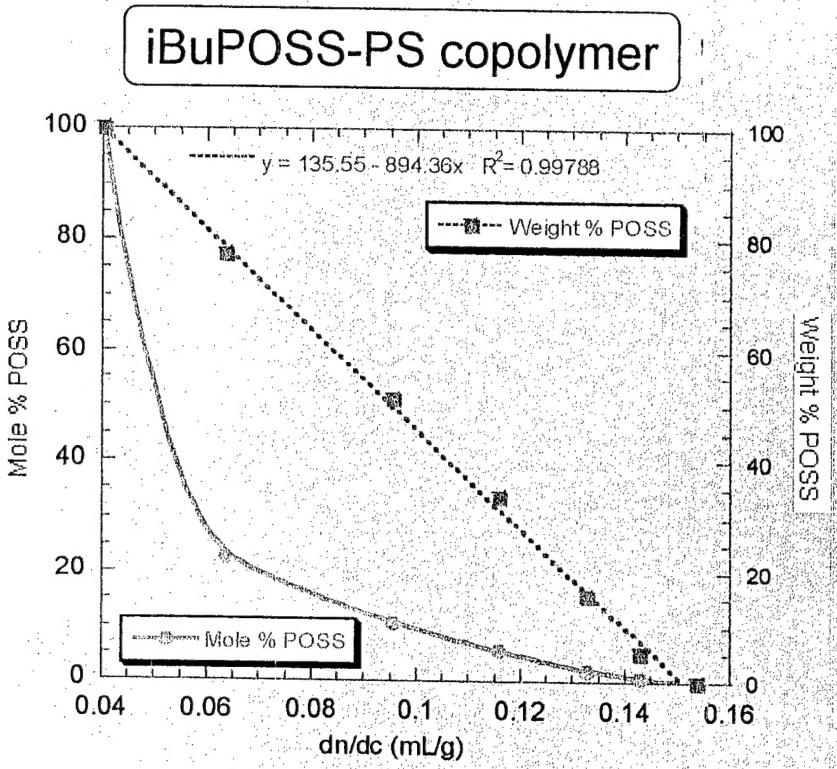
Y=0.1270x+1.4438
R^2 = 0.9995

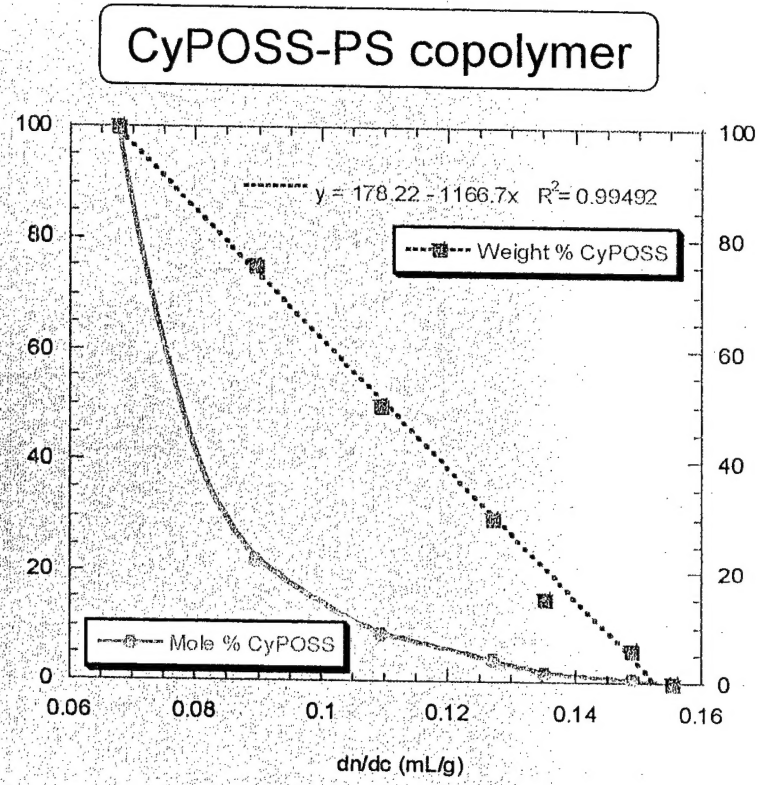
Y= 0.1094x+1.442
R^2 = 0.9994

Y= 0.0894x+1.444
R^2 = 0.9998

Y= 0.0676x+1.4442
R^2 = 0.9959

dn/dc vs. wt% and mole%





- Clearly, dn/dc is linear with respect to weight % POSS not mole % POSS; changes in refractive index are proportional to the volume occupied by the polymeric components. A typical POSS monomer is about 10X more massive than a typical organic monomer.
- Note that the dn/dc value decreases with increasing POSS incorporation.

Summary & Future Work

- There is a linear relationship between weight % POSS and the dn/dc of a styrene copolymer.

- To graph a dn/dc / weight % POSS relationship for any new POSS polymer it is reasonable to just measure the dn/dc values of the 0 and 100 % POSS polymer.

- We intend to prove this concept for other glassy (Acrylics) and rubbery (Norbornenes) POSS copolymers.

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